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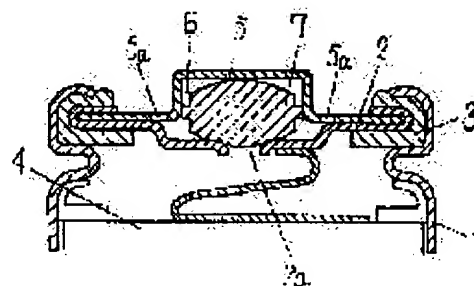
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## (54) SEALED BATTERY

## (57)Abstract:

PURPOSE: To provide the highly safe battery whose valve actuating pressure can be stably maintained over a long period of time by specifying an elastic valve body of a safety valve device in the battery having a battery vessel to house a power generating element and the safety valve device having the prescribed constitution.

CONSTITUTION: In the battery, a battery vessel 1 to house a power generating element and a safety valve device to seal an opening part of the battery vessel 1 are provided, and the safety valve device is composed of a disk-shaped sealing plate 2 having a gas ventilating hole 2a in a central part, an elastic valve body 7 which is arranged on the sealing plate 2 and blocks up the gas ventilating hole 2a and a cap-shaped positive electrode terminal 5 where the valve body 7 is positioned in a valve chamber 7. The elastic valve body 7 of the safety valve device in this battery is formed by cross-linking ethylene propylene rubber by mixing thermoplastic elastomer and ethylene propylene rubber together.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the closed mold cell which has relief valve equipment for raising the safety of a cell.

[0002]

[Description of the Prior Art] In recent years, the cell, especially the rechargeable battery in which a recharge is possible are used in the large field with the spread of various pocket devices. As a cell used for these devices, although the lead accumulator and the nickel cadmium battery have been used conventionally, nickel and the hydrogen battery, the rechargeable lithium-ion battery, etc. have newly been added.

[0003] In the cell in which these recharges are possible, sealing-ization is enabled by consuming the gas which occurs inside a cell with the so-called J. von Neumann method by the cell which is using water solutions, such as a lead accumulator, a nickel cadmium battery, and nickel, a hydrogen battery, as the electrolytic solution.

[0004] On the other hand, by cells using nonaqueous electrolyte, such as a rechargeable lithium-ion battery, sealing-ization has been attained by avoiding overcharge and overdischarge.

[0005] However, when it lapses into the abnormality situation resulting from failure of a battery charger, the misuse of a cell, an external short circuit, etc., the internal pressure of a cell may rise and it may result in a burst. In order to prevent the burst of this cell, the rechargeable battery is equipped with relief valve equipment so that the gas which occurred inside the cell may be emitted outside, when internal pressure exceeds the value set up beforehand.

[0006] Hereafter, the closed mold cell which has relief valve equipment is explained. Drawing 3 is up drawing of longitudinal section of a closed mold cell. In this drawing 3, the metal case 1 which is a cell container is carrying out wearing immobilization of the metal obturation plate 2 which formed gas air hole 2a in the upper part of a case 1 in the center section through the gasket 3 which plays the role of insulating and airtight maintenance by caulking processing. Although detailed illustration is not performed in the interior of the above-mentioned case 1, the generation-of-electrical-energy element 4 which consists a positive-electrode plate and a negative-electrode plate of superposition, a group of electrode wound spirally, and the alkali electrolytic solution through a separator is contained.

Furthermore, the cap-like positive-electrode terminal 5 used for the obturation plate 2 also in order to constitute relief valve equipment is formed. This positive-electrode terminal 5 is making the shape of a cap, and flueing opening 5a and a hole are formed in that part. The valve chest 6 is formed in the space surrounded by the positive-electrode terminal 5 and the obturation plate 2, and where the elastic valve element 7 is compressed into this valve chest 6, it builds. As a device of this elastic valve element 7, the thing using the elasticity of a metal spring or rubber is common.

[0007] In the closed mold cell which has the above configurations, when an internal pressure rise of the cell resulting from the inflow of the excessive charging current by failure of a battery charger, overdischarge which is accompanied by the polarity inversion arises, the gas which changed into the

high-pressure condition pushes up an elastic valve element, and is discharged from flueing opening 5a of the positive-electrode terminal 5.

[0008] Usually, when the internal pressure of a cell amounts to 10kg/cm<sup>2</sup> or more, the above-mentioned relief valve equipment used is set up so that gas may be emitted outside. Therefore, internal pressure rises as the gas absorption capacity of a negative electrode declines, when overcharge of extent without the rapid generation of gas is performed. If charge is suspended and the internal pressure of a cell falls satisfactory at this time even if the gas inside a cell is emitted outside, relief valve equipment returns to the original form, and he is trying to become usable again. Moreover, in order to make boosting charge possible, the rated allowable pressure of a relief valve may be heightened to about 20kg/cm<sup>2</sup>.

[0009]

[Problem(s) to be Solved by the Invention] Although the reduction of area of an elastic body is made small and the allowed value of internal pressure is raised by raising the degree of hardness of an elastic body, or enlarging compressibility, when the current beyond the set point flows into a cell and the abnormal occurrence of gas arises, the elimination rate from flueing opening cannot catch up with the generating rate of the gas inside a cell with the relief valve equipment which used such an elastic body. Therefore, cell internal pressure rises rapidly and has possibility of resulting in a burst. Moreover, an India rubber valve element filling heat expansion to the valve chest, it becoming impossible to maintain an original valve element moving function, and cell internal pressure rising like the above, and resulting in a burst by the temperature rise inside a cell, is also considered.

[0010] By JP,5-41204,A, in order to secure the safety at the time of investing a cell into fire, making one [ at least ] melting point of a packing material or the relief valve objects into 270 degrees C or less is indicated. However, an excessive current is impressed to a cell, if cell temperature amounts to about 100 degrees C, the hydrogen by which occlusion is carried out to the negative electrode will begin to be emitted, and the internal pressure of a cell rises rapidly and results in a burst. With the configuration indicated by the above-mentioned official report, it may be unable to correspond to the burst resulting from the influx of such an excessive current.

[0011] Furthermore, the indication about a point which uses thermoplastic elastomer olefin for an elastic valve element is also made by this official report. When cell temperature rises, a valve-action pressure declines too much by softening and the dissolution of thermoplastic elastomer, and a gas air hole will be in an open condition substantially. Consequently, the open air may flow in a cell, oxidation reaction with the hydrogen storing metal alloy of a negative electrode may be promoted, and a cell may be lit.

[0012] Moreover, the India rubber valve element which uses ethylene propylene rubber as a principal component mainly loses rubber elasticity gradually by oxidation. A setup of the valve-action pressure for securing dependability by aging of this rubber elasticity, over a long period of time [, such as exsorption suppression of the electrolytic solution, ], since the valve-action pressure of relief valve equipment declines was difficult.

[0013] This invention aims at offering the closed mold cell which has relief valve equipment which can solve the problem of the safety which secures the dependability which can carry out stable maintenance of the valve-action pressure over a long period of time, and is produced by change of the internal pressure accompanying the rapid temperature rise of a cell.

[0014]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the closed mold cell of this invention mixes thermoplastic elastomer (hereafter referred to as TPE), and ethylene propylene rubber (hereafter referred to as EPDM), sets the valve-action pressure of the relief valve equipment in 100-120 degrees C as 4-8kg/cm<sup>2</sup>, and makes this valve-action pressure hold to 250 degrees C to the elastic valve element built in relief valve equipment using what carried out arch forming of said EPDM.

[0015]

[Function] TPE consists of two phases of the hard phase which gives thermoplasticity, and the elasticity phase which gives elasticity. When the high current beyond the set point flows, cell temperature rises by this, the abnormal occurrence of gas arises, and the hard phase which forms this TPE melts, the working pressure as an elastic valve element declines, and the elimination rate from flueing opening becomes

large substantially. The rise of cell internal pressure is suppressed because an elimination rate follows an internal generation-of-gas rate, and the burst of a cell can be prevented.

[0016] Moreover, since EPDM is constructing the bridge in TPE, and after mixing and itself, even if TPE softens it at the time of an elevated temperature, since the structure of cross linkage of EPDM is maintained, too much fall of a valve-action pressure is prevented, and the open air does not flow in a cell. Thereby, nickel and a hydrogen battery, a lithium cell, etc. can prevent ignition resulting from the inflow of the air from the outside, or oxygen especially.

[0017] Furthermore, since an elastic valve element is the mixture of TPE and EPDM, it is hard to permeate the interior, destruction of the structure of cross linkage of EPDM accompanying degradation by oxidation is controlled, and an oxygen molecule becomes securable [ the stabilization over the long period of time of a valve-action pressure, i.e., dependability ] from the front face of an elastic valve element.

[0018] in addition, the mixing ratio of EPDM and TPE -- with 1:2 [ or more ], about a rate, the fall of the valve-action pressure in operating temperature limits can usually be prevented according to the oxidation depressor effect of EPDM by TPE. On the other hand, a setup of a valve-action pressure is also easy, without the degree of hardness of an elastic valve element becoming large too much by the increment in a hard phase with 1:4 [ or less ].

[0019] therefore, the mixing ratio of EPDM and TPE -- as for a rate, 1:2-1:4 are desirable.

[0020]

[Example] Hereafter, one example of this invention is explained, referring to a drawing.

[0021] (Example 1) the relief valve equipment shown in drawing 3 -- constituting -- the mixing ratio of EPDM and TPE -- examination about a rate was performed.

[0022] EPDM and TPE were mixed at a rate of the weight ratios 1:2, 1:3, and 1:4, the elastic valve element which carried out bridge formation processing of the EPDM part was created, respectively, and the relief valve equipments A, B, and C of this invention article using these valve elements were constituted.

[0023] Moreover, the relief valve equipment E using the elastic valve element which created only from EPDM the insurance section valve gear D which set the ratio of EPDM of the above-mentioned elastic valve element and TPE to 1:1 as a conventional example as an example of a comparison was constituted.

[0024] Examination about the heat-resistant degradation property of an elastic valve element was performed using five kinds of relief valve equipments of above-mentioned A-E. After carrying out fixed period preservation under the environment of 65 degrees C of ambient temperature, the valve-action pressure was measured. The relation between a retention period and a valve working pressure maintenance factor is shown in drawing 1 . Compared with the relief valve equipment E only using the conventional EPDM, the degradation degree by the heat of the relief valve equipments A, B, C, and D which mixed EPDM and TPE is small so that clearly from this drawing 1 . Moreover, as for coincidence, the weight ratio of TPE to EPDM also understands that thermal resistance improves by enlarging. the mixing ratio of EPDM and TPE -- with 1:2 [ or more / of this invention ], it is clear about a rate that the fall of valve working pressure can be prevented according to the oxidation depressor effect of EPDM by TPE.

[0025] Since bridge formation processing of the EPDM is carried out after the relief valve equipment of the closed mold cell of this invention mixes EPDM and TPE for an elastic valve element by the weight ratio of 1:2-1:4 from this, the fall of the valve working pressure by degradation of EPDM can be prevented, and relief valve equipment reliable over a long period of time can be offered.

[0026] (Example 2) EPDM and TPE of this invention were mixed by the weight ratio of 1:3, the closed mold nickel and the hydrogen battery of A size of nominal capacity 1600mAh were produced using the relief valve equipment constituted by the elastic valve element which carried out bridge formation processing of the EPDM part, and this cell was used as Cell F.

[0027] On the other hand, the insurance section valve gear which used only EPDM for the conventional elastic valve element as an example of a comparison was used, and the nickel and the hydrogen battery

produced like the above were used as Cell G. Moreover, the cell H using the relief valve equipment which has the elastic valve element which consists only of TPE was constituted.

[0028] the current of 8A (5C) which assumed poor control of a battery charger at a time for three kinds of cells of above-mentioned F-H about 20 cels of each -- charge -- carrying out -- cell temperature -- measuring -- at the same time -- a burst and ignition -- having resulted -- a cell -- counting -- it carried out. The result is shown in Table 1.

[0029]

[Table 1]

	電池破裂数	電池発火数
電池 F	0 個	0 個
電池 G	8 個	0 個
電池 H	0 個	3 個

[0030] Although the current excessive at the time of charge flowed into the cell, cell temperature rose and gas leakage occurred from the interior of a cell by the cell F by this invention, the cell which resulted in a burst and ignition was not accepted.

[0031] On the other hand, by Cell G, when cell temperature reached near 150 degree C, four cels exploded in one cel one cel and near 170 degree C, and exploded two cels and near 200 degree C near 180 degree C. Each of these changed into the condition that the obturation plate separated from the obturation section of metal casing.

[0032] On the other hand, by Cell H, although the cell which resulted in a burst was not able to be checked, when cell temperature rose to near 230 degree C, ignition was accepted from three cels. In addition, even if each cell of Cells F and G performed charge with an excessive current, it did not ignite.

[0033] The result of having measured fluctuation of the valve-action pressure value of the safety device by the temperature rise of a cell about three kinds of cells to above-mentioned F-H is shown in drawing 2.

[0034] The valve-action pressure of Cell F is declining sharply from near 100 degree C, when the rise of cell temperature is followed and TPE is softened or eluted. In connection with this, the gas elimination rate from flueing opening increases. However, the lock out function of an elastic valve element is maintained by EPDM to which arch forming of the 250 degrees C was carried out from 120 degrees C which the elution of TPE calmed down, and the almost fixed valve-action pressure is held.

[0035] On the other hand, the valve-action pressure of the relief valve equipment of Cell G is rising gently from near 100 degree C by heat expansion of EPDM. This shows that the gas elimination rate from flueing opening is falling. On the other hand, although, as for the valve-action pressure of the relief valve equipment of Cell H, softening or elution of TPE advances by the temperature rise and the gas elimination rate goes up, it is clear to have stopped showing the lock out function of an elastic valve element near 250 degree C.

[0036] The effectiveness which maintains the safe elimination rate of the gas which occurred inside the such hot cell, and prevents the inflow of the atmospheric air into a cell is acquired by holding 4-8kg/cm<sup>2</sup> working pressure, as a result of performing the above-mentioned various examination.

[0037] When the abnormal occurrence of gas arises inside a cell by considering an elastic valve element as the configuration to which arch forming of the EPDM with which TPE was mixed was carried out, and the resinous principle which forms TPE begins to soften or melt, the working pressure as an elastic

valve element declines, and the relief valve equipment of the closed mold cell of this invention presses down the rise of cell internal pressure, and can prevent the burst of a cell. Furthermore, since EPDM over which the bridge was constructed has enclosed and covered TPE, and the lock out function of an elastic valve element is maintainable, the fall of too much valve-action pressure is controlled. Thereby, ignition of nickel and a hydrogen battery can be prevented especially.

[0038]

[Effect of the Invention] As mentioned above, according to this invention, by maintaining a valve-action pressure to stability over a long period of time, it can respond to a sudden rise of the cell internal pressure accompanying a rapid temperature rise, and it not only secures dependability, but can offer a closed mold cell with the relief valve equipment with high safety which prevents ignition of a cell further.

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[Translation done.]